

⑩



Europäisches Patentamt

European Patent Office

Office européen des brevets

⑪ Publication number:

**0 197 662**

**B1**

⑫

## EUROPEAN PATENT SPECIFICATION

⑬ Date of publication of patent specification: 31.10.90

⑭ Int. Cl.<sup>5</sup>: C 09 J 7/00, C 09 J 133/08

⑮ Application number: 86301693.7

⑯ Date of filing: 10.03.86

⑰ Pressure-sensitive adhesive tape having a substantially tack-free surface.

⑱ Priority: 15.03.85 US 712277

⑲ Date of publication of application:  
15.10.86 Bulletin 86/42

⑳ Publication of the grant of the patent:  
31.10.90 Bulletin 90/44

㉑ Designated Contracting States:  
DE FR GB IT

㉒ References cited:  
EP-A-0 121 430  
WO-A-79/01013  
DE-A-2 355 364  
FR-A-2 040 310  
US-A-3 677 985

㉓ Proprietor: MINNESOTA MINING AND  
MANUFACTURING COMPANY  
3M Center, P.O. Box 33427  
St. Paul Minnesota 55133 (US)

㉔ Inventor: Larimore, Franklin C. c/o Minnesota  
Mining and  
Manufac. Comp. 2501 Hudson Road P.O. Box  
33427  
St. Paul Minnesota 55133-3427 (US)  
Inventor: Sinclair, Robert A. c/o Minnesota  
Mining and  
Manufac. Comp. 2501 Hudson Road P.O. Box  
33427  
St. Paul Minnesota 55133-3427 (US)

㉕ Representative: Baillie, Iain Cameron et al  
c/o Ladas & Parry Isartorplatz 5  
D-8000 München 2 (DE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

**EP 0 197 662 B1**

## Description

## Field of the Invention

The invention concerns pressure-sensitive adhesive tape which normally is produced in wide widths that may be sold as such but usually are split to narrow widths to be wound up for convenient storage and shipment. The invention especially concerns pressure-sensitive adhesive tapes which transmit water vapor, a property advantageous for medical purposes.

## Background Art

Known pressure-sensitive adhesive tapes are comprised of two distinct layers, namely, an adhesive layer and a backing layer which supports the adhesive layer. When the adhesive and backing layers are inseparably united, the backing usually is responsible for more than half of the cost of the tape. In tapes made for medical purposes, the backing can be several times more expensive than the adhesive layer. Upon applying a pressure-sensitive adhesive tape to a compound surface, the backing may cause the tape to pucker and hence become poorly adhered. Where a compound surface flexes, for example a person's knee, the tape may loosen and fall off. While these problems can be lessened by employing highly conformable backings, it is believed no pressure-sensitive adhesive tape has a utilitarian backing of reasonable cost that has a conformability even approaching that of a pressure-sensitive adhesive layer.

## Other Prior Art

Possibly the most versatile class of pressure-sensitive adhesive tape is disclosed in U.S. Patent No. Re. 24,906 (Ulrich), the adhesive layers of which are copolymers of (a) one or more acrylic acid esters of non-tertiary alkyl alcohol having a chain of 1 to 14 carbon atoms, and (b) one or more copolymerizable monomers such as the vinyl carboxylic acid monomers acrylic acid, methacrylic acid, and itaconic acid. This class of pressure-sensitive adhesives has a host of uses and is especially useful for medical purposes since, among other reasons, they need contain no tackifiers or other materials which might cause allergic reactions.

U.S. Patent No. 3,740,366 (Sanderson et al.) reports that when a carboxyl-containing, pressure-sensitive adhesive polymer of the Ulrich patent is crosslinked between carboxyl groups by polyvalent metal cations, improved shear resistance is obtained without appreciable loss of tackiness if the polymer is "derived from up to 4.5% of the total monomers of an alpha, beta-ethylenically unsaturated carboxylic acid" (col. 1, lines 64-66). At higher carboxylic acid proportions, polymers would appreciably lose tackiness and become increasingly less soft and compliant unless restricted amounts of polyvalent metal cations were employed.

A class of pressure-sensitive adhesive tapes which are closely related to those of the Ulrich patent are disclosed in U.S. Patent No. 3,865,770 (Blake), their adhesive layers being copolymers of (a) about 90-20 parts by weight acrylic acid ester of non-tertiary alkyl alcohol having a chain of 1 to 14 carbon atoms, (b) about 10-80 parts by weight copolymerizable vinyl carboxylic acid monomer, some of the carboxyl groups of which have been neutralized by reaction with an alkanolamine, and (c) tack-promoting material in an amount sufficient to provide a certain tackiness. Pressure-sensitive adhesive tapes of this class are water-dispersible or water-soluble and also display good tack and heat stability, thus being especially useful for making splices in papermaking and printing operations. Tapes of this class also are suitable for biomedical electrodes, because of their low electrical impedance and good adhesion and precise conformability to skin.

In another class of pressure-sensitive adhesive tapes, the adhesive layers are made by polymerizing an adhesive precursor comprising (1) a water-soluble polyhydric alcohol which is a liquid at about 20°C, (2) an ionic unsaturated free radically polymerizable material which is soluble in said polyhydric alcohol, e.g., acrylic acid, (3) a free radical initiator soluble in said polyhydric alcohol, and (4) a crosslinking agent of a multifunctional unsaturated free radically polymerizable material soluble in said polyhydric alcohol. As disclosed in U.S. Patent Application Serial No. 514,950 filed July 18, 1983 (Engel), a coating of said precursor can be polymerized to a pressure-sensitive adhesive state, preferably by exposure to ultraviolet radiation. The resulting pressure-sensitive adhesive layer retains a significant amount of water which affords moderate electrical conductivity that can be enhanced by adding electrolytes to the water. Because of their electrical conductivity and because they have good adhesion and precise conformability to skin, these adhesive layers are used in biomedical electrodes which are adhesively attached to the human skin.

## Disclosure of Invention

In one aspect the invention provides pressure-sensitive adhesive tape, the adhesive layer of which comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, the polymer along at least one surface of the layer being substantially tack-free by having been crosslinked between carboxyl groups by polyvalent cations.

The invention also provides pressure-sensitive adhesive tape, the adhesive layer of which comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, the polymer having tiny spaced mounds along one broad surface of the layer at which carboxyl groups of the polymer have been crosslinked by polyvalent cations while leaving the spacings between the mounds uncrosslinked and tacky.

The pressure-sensitive adhesive tape of the invention need not have a backing in that the adhesive layer can have adequate strength to permit it to be used without a backing. The adhesive layer of a preferred tape of the invention has one broad, tacky and pressure-sensitive face and one broad, substantially tack-free face which can serve the function of an ordinary backing and thus eliminate the expense of a backing. When a separate backing member is eliminated, the novel tape has marvelous conformability.

The portion of the adhesive layer which is crosslinked has greatly increased tensile strength and much reduced extensibility.

When the polymer is substantially tack-free across one of the broad surfaces of the adhesive layer, that surface may optionally be covered with a low-adhesion backsize coating, thus permitting the adhesive layer to be wound (without a backing) directly upon itself in roll form for convenient storage and shipment and later unwound and dispensed as are other pressure-sensitive adhesive tapes. Even without a low-adhesion backsize coating, some such tapes can be wound upon themselves and later unwound without delaminating, especially if not stored for prolonged periods of time.

Both broad surfaces of some other preferred pressure-sensitive adhesive tapes of the invention are tacky, and the polymer is crosslinked only along one or both edges of the adhesive layer. A substantially tack-free edge surface eliminates problems such as oozing and dirtiness that have been disturbing in the use of some prior pressure-sensitive adhesive tapes. When both of its broad surfaces are tacky and only one or both edges of the adhesive layer of the novel pressure-sensitive adhesive tape are substantially tack-free, it should have a backing which may or may not have a low-adhesion surface to permit the adhesive layer to be removed for such purposes as to join two substrates adhesively.

A preferred pressure-sensitive adhesive for the novel tape comprises a copolymer of (a) from 88 to 97 parts of one or more acrylic acid esters of non-tertiary alkyl alcohol having a chain of 1 to 14 carbon atoms, and (b) correspondingly 12 to 3 parts of one or more copolymerizable monomers such as the vinyl carboxylic acid monomers acrylic acid, methacrylic acid, and itaconic acid. Preferably, the average chain of the alcohol has 4 to 12 carbon atoms. Such a copolymer can both be aggressively tacky and have high cohesive strength, retaining those properties after being stored in tape form for years at ordinary room temperatures. Furthermore, pressure-sensitive adhesive layers of these polymers have good water-vapor transmission, allowing them to remain in contact with the human skin for prolonged periods without injury. The crosslinking of such a polymer along a broad surface of the adhesive layer in tapes of the invention provides even better water-vapor transmission.

Another preferred pressure-sensitive adhesive for a tape of the invention comprises copolymers of (a) 90—20 parts by weight acrylic acid ester of non-tertiary alkyl alcohol having a chain of 1 to 14 carbon atoms, (b) 10—80 parts by weight copolymerizable vinyl carboxylic acid monomer such as acrylic acid, methacrylic acid, and itaconic acid, some of the carboxy groups of which have been neutralized by reaction with an alkanolamine, and (c) tack-promoting material in an amount sufficient to provide good tackiness.

A third preferred pressure-sensitive adhesive for a tape of the invention may be prepared as taught in the above-cited U.S. Patent Application 514,950. That adhesive comprises a polymer of an ionic unsaturated free radically polymerized material such as acrylic acid combined with a crosslinking agent and free radical initiator (as outlined above), which are polymerized from an adhesive precursor containing a polyhydric alcohol such as glycerol. It is believed that the polyhydric alcohol hydrogen bonds to the other materials and so may be considered to be an integral part of the polymeric adhesive.

Further preferred embodiments are defined in the dependent claims.

In another aspect of the invention provides a method of making substantially tack-free at least one surface of a pressure-sensitive adhesive layer while leaving another surface tacky, which adhesive layer comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, said method comprising applying to said one surface a non-aqueous medium containing a Lewis acid, a polyvalent cation, or a polyvalent organo-metallic complex or salt to crosslink the polymer along said at least one surface to a substantially tack-free state.

The invention also provides a method of producing substantially tack-free separated mounds on at least one broad surface of a pressure-sensitive adhesive layer while leaving the spacings between the mounds tacky, which adhesive layer comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, said method comprising applying to the adhesive layer a dot pattern of a non-aqueous medium containing a Lewis acid, a polyvalent cation, or a polyvalent organo-metallic complex or salt to form the mounds and crosslink the polymer at the mounds to a substantially tack-free state.

The Lewis acid, polyvalent cation, or polyvalent organo-metallic complex or salt may be applied either with or without a non-aqueous solvent, which does not disrupt the adhesive layer. When no solvent is used, the crosslinking penetration will depend upon the fluidity and viscosity of the polymer being crosslinked. When a solvent is used, the polyvalent metal or other cations can penetrate to a considerable depth quite rapidly, but the depth of crosslinking can be controlled either by limiting the amount of cations applied or by removing unreacted cations, e.g., by washing, by squeezing, or by an air jet. When the tape includes a backing to which the adhesive layer is permanently adhered, crosslinking at one broad surface on the edge surfaces can be achieved by momentarily dipping the tape into a solution of Lewis acid, polyvalent cation, or organo-metallic complex or salt.

Solvents other than water are used because diffusion of the cations into the adhesive layer from an

aqueous system would be inhibited by a hydrophobic barrier produced by crosslinking of the surface carboxyl groups. When using a solvent, it preferably is readily miscible with water and relatively polar, preferably an alcohol such as ethanol or isopropanol. Other useful water-miscible solvents include acetone, methyl ethyl ketone, ethyl acetate, and N,N-dimethylformamide. When using water-miscible solvents to carry the polyvalent cations, the depth of crosslinking can be economically controlled by washing with water.

Useful Lewis acids includes  $ZnCl_2$ ,  $TiCl_4$ ,  $FeCl_3$ , and  $AlCl_3$ . Solutions of  $AlCl_3$  should not be exposed to the atmosphere except during use, or absorbed water may interfere with penetration of the aluminum cations and also result in a powdery deposit at the surface being treated. However,  $AlCl_3$  does not color the adhesive as do some other Lewis acids such as  $FeCl_3$ . Because of their low cost and nontoxicity, the Lewis acids named above are preferred. For uses in which any corrosion must be avoided, a polyvalent organo-metallic complex or salt is preferred to a Lewis acid. Exemplary complexes and salts include zinc octanoate, calcium acetate, aluminum triisopropoxide, tetra-n-butyl titanate, titanium acetyl acetonate, and lactic acid titanium chelates.

The crosslinking of the polymer along a broad surface of the adhesive layer affords greatly improved strength, thus allowing the adhesive layer to be used without a backing. However, in tapes of the invention which have no backings, greatly enhanced strength and integrity can be provided by a tissue-like scrim, preferably of cellulose or nylon, embedded in and coextensive with said adhesive layer. Such a scrim does not substantially lessen the conformability of the adhesive layer.

When the polymer is crosslinked along a broad surface of the adhesive layer, this affords a leathery or silk-like feel. Microscopic examination reveals a wrinkling of the adhesive layer which cannot be detected by the naked eye. The crosslinking greatly reduces stretchability, so that when the tape is microscopically examined after being moderately stretched, crosslinked areas can be ruptured without breaking the underlying tacky adhesive, thus confirming that the adhesive layer has not been crosslinked adjacent that tacky surface while being crosslinked adjacent the other broad surface. The respectively tacky and substantially tack-free nature of those surfaces likewise confirms this.

Both broad surfaces of the adhesive layer may be treated to become crosslinked to a minor portion of the layer thickness. The adhesive layer may then be stretched to fracture the crosslinked portion, thus exposing the still-tacky core by which the adhesive layer can be adhered to a substrate or used to adhesively bond two substrates together.

The embodiment of the invention in which the polymer is crosslinked in tiny, separated areas along one broad surface of the adhesive layer can be made by using a half-tone printing plate to print tiny dots onto the surface with a solution of a Lewis acid, polyvalent cations, or a polyvalent organo-metallic complex or salt. Crosslinking initiated where the polyvalent cations contact the polymer puckers the adhesive layer to create microscopic mounds which are substantially tack-free and are separated by narrow tacky areas. The surface of the adhesive layer thus becomes virtually nontacky under light pressure, but adhesive bonds can be made by pressing the surface against a substrate. The strength of those bonds is dependent upon the pressing force.

#### The Drawing

In the drawing,

Fig. 1 is a scanning electron micrograph of a magnification of 200x showing a broad surface of a tape of the invention which has been moderately stretched to break the crosslinked portion of its adhesive layer without breaking the uncrosslinked portion; and

Fig. 2 is a similar micrograph of the same tape at a magnification of 5000x.

In the areas 10 of Fig. 1, the portion of the adhesive layer along the broad surface being viewed has been crosslinked, thus puckering that surface which originally has been relatively smooth. Stretching of the tape has produced rifts in the crosslinked portion, revealing areas 12 where uncrosslinked adhesive has elongated to bridge the rifts. As better seen in Fig. 2, the crosslinking extends uniformly into the adhesive layer. The nonuniform depth of the crosslinked portion is attributed to the resulting puckering.

In the following examples, all parts are by weight unless otherwise noted.

#### Example 1

A cellulose scrim (8-pound "Crystex® Tissue" supplied by Crystal Mills, Middletown, Ohio) has been coated on both sides with a pressure-sensitive adhesive polymer of the type disclosed in U.S. Patent No. 3,865,770 and prepared from

	Parts
n-butyl acrylate	400
acrylic acid	133
N-methyl diethanolamine	266
rosin tackifier	160
polyethylene glycol monophenyl ether (ave. mol. wgt. 270)	106

## EP 0 197 662 B1

The double-coated scrim-reinforced adhesive layer had a thickness of about 0.09 mm and was carried by a coated paper backing having a release surface. Carboxyl groups comprised 7.8% of the weight of the adhesive. Strips (12 × 2.5 cm) of this paper-backed tape were immersed in 0.05M FeCl<sub>3</sub>·6H<sub>2</sub>O in absolute ethanol and immediately dipped momentarily into water to wash away any unreacted ferric chloride. After drying in air at room temperature, the strips were peeled from the coated paper backing and tested for tensile strength in an Instron Tensile Tester under ASTM Test Method D 882—75b, with the following results:

10

	Tape	Immersion time (min.)	Elongation at max. load (%)	Tensile strength (kPa)
15	A	0	5	2700
	B	0.25	10	3300
	C	1	10	2950
20	D	2	15	3600
	E	5	10	5900
	F	15	10	8550
25	G	30	10	10350
	H	60	10	13550

30

The exposed surface of each of Tapes B—H had a beige color and was completely tack-free to the touch. The exposed surface of Tape A and the underlying surfaces of each of Tapes A—F were aggressively tacky to the touch and no difference in their tackiness was apparent. The underlying surface of Tape G had reduced tackiness, and that of Tape H was almost tack-free, indicating that substantially its entire adhesive layer had become crosslinked by the metal cations.

35

The adhesive layers of Tapes E and F had adequate strength to be marketed without backings and could be wound upon themselves in roll form for convenient storage and shipment, preferably after first applying low-adhesion backsize coatings to their tack-free surfaces.

40

Two other strips of the paper-backed, double-coated resin were immersed in the 0.05M FeCl<sub>3</sub>·6H<sub>2</sub>O solution, one momentarily and the other for two hours, and then dipped into water. After drying, the backings were discarded, and the modified adhesive layers were tested for water vapor transmission by ASTM Test Method E96—80, Method 3.2. The transmission of each was at least 328 g/m<sup>2</sup>/hour, more than adequate for surgical tape use.

45

### Example 2

Strips of the tape used in Example 1 were momentarily dipped into a 5% solution of anhydrous aluminum trichloride in anhydrous ethanol and allowed to dry at room temperature without being washed. The exposed surfaces of the dried strips had become completely tack-free to the touch. When peeled from the paper backing, the underlying surface of the adhesive layer appeared to be as aggressively tacky as the surfaces of Tape A. The adhesive layer was clear and colorless. After another of the modified strips were immersed in water at 80°C for more than one-half hour and then allowed to dry at room temperature, its adhesive layer appeared to be unchanged.

50

### Example 3

55

A strip of the tape used in Example 1 was immersed for 30 seconds in a solution of 5% by weight zinc chloride in anhydrous ethanol and immediately washed in ethanol. After drying, its exposed surface was tack-free to the touch, but when rubbed, some thickness was evident. The underlying surface of the adhesive layer was as tacky as Tape A.

60

Another strip of the tape used in Example 1 was immersed to half of its length in the same solution for 30 seconds, and then the entire strip was immediately immersed in water at about 20°C. After about 5 minutes, the untreated section of the tape had become swollen and translucent, whereas the treated section was unchanged. After about one hour, the edge of the treated section had swelled slightly.

65

A third strip of the tape used in Example 1 was immersed to half its length in the same solution for 30 seconds and then immediately totally immersed in a 5% solution of sodium chloride in water at about 20°C. Neither section of this strip showed any swelling or opacity after one hour.

## EP 0 197 662 B1

### Example 4

A strip of the tape used in Example 1 was immersed in a solution of 1.1 g of zinc octanoate in 10 ml ethanol. After 5 minutes, the strip was allowed to dry without being washed. The exposed surface of the dried strip was completely tack-free to the touch, while the underlying surface of its adhesive layer appeared to be as tacky as Tape A.

### Example 5

A pressure-sensitive adhesive tape was prepared by coating onto the release surface of a coated paper backing a mixture of 90 parts of isooctyl acrylate and 10 parts of acrylic acid, which mixture had been partially polymerized to a coatable state. After adding a photoinitiator and covering the coating with a releasable transparent plastic film to exclude air, the coating was polymerized to a pressure-sensitive adhesive state by exposure to ultraviolet radiation. The thickness of the adhesive layer of the resulting tape was about 250 micrometers. Carboxyl groups comprised about 6.2% of the weight of the adhesive layer. After removing the transparent plastic film, one strip of the paper-backed tape was momentarily immersed in 0.05M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in ethanol, and another in 5% anhydrous  $\text{AlCl}_3$  in ethanol and then dipped in ethanol to remove unreacted metal cations. After being allowed to dry, the exposed surface of the adhesive layer of each strip was completely tack-free, indicating crosslinking along that surface, and the underlying surface of each adhesive layer appeared to be as tacky to the touch as was Tape A.

The adhesive layer of a strip which had been immersed in the ferric chloride solution was peeled from the paper backing and stretched by hand to break the crosslinked portion while leaving the uncrosslinked portion unbroken. Micrographs of the stretched adhesive layer are shown in Figs. 1 and 2 of the drawings. The tack-free, crosslinked portion was from 4 to 10 micrometers in thickness, about 2 to 4% of the total thickness of the adhesive layer.

### Example 6

Used in this example was a tape which was the same as that used in Example 5 except that its adhesive layer had a thickness of about 125 micrometers. While strips of the tape were in a vacuum ( $10^{-5}$  mm of Hg), they were allowed to equilibrate with pure  $\text{TiCl}_4$  vapor at room temperature, one for 10 minutes and the other for 30 minutes.

An exposed adhesive surface of the strip thus treated for 10 minutes was almost tack-free but was slightly tacky to the touch. The exposed adhesive surface of the strip treated for 30 minutes was completely tack-free. The underlying surface of the adhesive layer of each strip was aggressively tacky, having been unchanged by the treatment. Both treated adhesive layers were stretchy and conformable and unchanged in these respects compared to untreated adhesive layers. The treatment did not change the clear, colorless, glossy appearance of the adhesive layers when examined with the naked eye.

### Example 7

The exposed adhesive surface of a roll of the starting tape used in Example 5 was printed with a 0.05M solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in ethanol using a demonstration half-tone flexographic printing plate (ByChrome Co., Inc., Columbus, Ohio) on a rotary press. The largest dots on the printing plate had a diameter of 290 micrometers and a spacing of 250 micrometers. The smallest dots had a diameter of 65 micrometers and a spacing of 170 micrometers. Microscopic examination showed tiny, beige-colored, tack-free mounds of approximately the diameter of the corresponding dots of the printing plate. The face of the printed tape was virtually nontacky when lightly touched but felt rather tacky under greater fingertip pressure. When a piece of the printed adhesive layer was stretched, the size of each mound remained unchanged while the spacings between the mounds was enlarged, and the face of the printed adhesive layer then felt quite tacky when lightly touched. When another piece of the printed adhesive layer was lightly pressed against a substrate, it became lightly adhered, and the degree of adhesion increased under increased pressure until the printed adhesive layer became strongly adhered to the substrate.

### Example 8

A tape had a cellulose acetate backing and a pressure-sensitive adhesive layer consisting of a copolymer of 95 parts of isooctyl acrylate and 5 parts of acrylic acid, of which polymer carboxyl groups comprised about 3.1% of its weight. One strip of this tape was momentarily immersed in 0.05M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in ethanol and another in anhydrous  $\text{AlCl}_3$  in ethanol, and then dipped in ethanol. After being allowed to dry, the exposed adhesive surface of each strip was only slightly tacky to the touch, whereas the underlying surface of the adhesive layer appeared to be as tacky to the touch as the surfaces of Tape A. Upon rubbing the exposed surface of the treated adhesive layer of each strip, it became very tacky to the touch.

### Example 9

A tape had a paper backing having a silicone resin release coating over which a pressure-sensitive adhesive layer consisting of a copolymer of isooctyl acrylate and acrylic acid in 94.6 ratio had been coated from a 22% solution of heptane and isopropyl alcohol (70:30) and heated at gradually increasing temperatures to provide a dry adhesive weight of 81.5 mg/m<sup>2</sup>. The thickness of the dried adhesive layer was about 0.2 mm.

## EP 0 197 662 B1

Onto the uncoated surface of the paper backing was applied a barrier layer which was a terpolymer of 92 parts vinyl chloride, 6 parts vinyl acetate and 2 parts vinyl alcohol ("VAGH #1" supplied by Union Carbide Chemicals Co.). The barrier layer comprised about 2 grains per square inches (84 mg/m<sup>2</sup>). A silicone low-adhesion backsizing was coated over the barrier layer.

Pieces were then laid up in a slab and guillotined into pads, each having multiple long, narrow strips. The long edges of the strips were then treated with tetra-n-butyl titanate ("Tyzor"® TBT sold by Union Carbide Chemicals Co.) to crosslink the pressure-sensitive adhesive along both edges of the strips to detackify the adhesive, thus reducing the migration of the adhesive from the edges of the pads and also reducing soiling of the edges of the pad during storage and use.

### Example 10

A coating of the following adhesive precursor solution was polymerized to provide a pressure-sensitive adhesive layer which is useful for attaching biomedical electrodes to the skin:

	Parts
Glycerol	62
Acrylic acid	22
Water	13
Triethyleneglycol-bis-methacrylate	0.06
2,2-dimethoxy-2-phenyl acetophenone photoinitiator ("Irgacure" 651)	0.07

plus 3 parts of salts, e.g., to enhance electrical conductivity.

In accordance with teachings of the above-cited U.S. Patent Application Serial No. 514,950, the solution was knife-coated onto silicone coated paper which was then passed through an inert chamber (N<sub>2</sub> atmosphere) under a bank of UV lamps to polymerize the coating to a pressure-sensitive adhesive state. Carboxyl groups comprised about 13.8% by weight of the polymerized coating which had a thickness of about 0.8 mm.

A strip of this tape was momentarily immersed in 0.05M FeCl<sub>3</sub>·6H<sub>2</sub>O in ethanol, and another strip was momentarily immersed in 0.05M FeCl<sub>3</sub>·6H<sub>2</sub>O in water. After drying, the exposed adhesive surface of each strip was completely tack-free, and the underlying surface of the adhesive layer was highly tacky and unchanged in tackiness.

### Example 11

Tape was prepared as in Example 1 except that its backing was biaxially-oriented poly(ethylene terephthalate) filmed coated with a conductive silver paint and its adhesive precursor was:

	Parts
Glycerol	66.7
Acrylic acid	15.6
Water	12.8
Triethyleneglycol-bis-methacrylate	0.37
2,2-dimethoxy-2-phenyl acetophenone	0.07

plus 4.5 parts of salts. The adhesive layer of the tape had a thickness of 800 micrometers.

A number of strips of this tape were immersed in 0.05M FeCl<sub>3</sub>·6H<sub>2</sub>O in ethanol for periods of time given below and then immediately dipped into water. After drying, the exposed adhesive surface of each strip was tack-free, and the underlying surface of its adhesive layer was aggressively tacky to the touch. No differences in their tackiness was apparent.

After freezing and breaking each strip, the broken edge was microscopically examined to determine the thickness of their crosslinked portions as follows:

# EP 0 197 662 B1

	After immersion for	Depth of Crosslinking (micrometers)
5	10 seconds	220
	20 seconds	220
10	40 seconds	550
	80 seconds	740

## Claims

1. Pressure-sensitive adhesive tape, the adhesive layer of which comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, the polymer along at least one surface of the layer being substantially tack-free by having been crosslinked between carboxyl groups by polyvalent cations.
2. Pressure-sensitive adhesive tape, the adhesive layer of which comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, the polymer having tiny spaced mounds along one broad surface of the layer at which carboxyl groups of the polymer have been crosslinked by polyvalent cations while leaving the spacings between the mounds uncrosslinked and tacky.
3. Pressure-sensitive adhesive tape as claimed in claim 1 wherein at least one broad surface of the layer is uncrosslinked and tacky.
4. Pressure-sensitive adhesive tape as claimed in any preceding claim wherein an edge surface of the layer is crosslinked by said cations and substantially tack-free.
5. Pressure-sensitive adhesive tape as claimed in any preceding claim wherein at least one broad surface of the layer is crosslinked by said cations and substantially tack-free.
6. Pressure-sensitive adhesive tape as claimed in claim 5 wherein said other broad surface is completely tack-free and the adhesive layer is wound upon itself in roll form without a backing.
7. Pressure-sensitive adhesive tape as claimed in claim 5 or claim 6 having a low-adhesion backsize coating covering said broad tack-free surface of the adhesive layer.
8. Pressure-sensitive adhesive tape as claimed in any of claims 5, 6 and 7 the adhesive layer of which has been crosslinked to a substantially tack-free state at both broad surfaces, leaving a still-tacky core which can be exposed by stretching the adhesive layer to fracture the crosslinked portions without breaking the tacky core.
9. Pressure-sensitive adhesive tape as claimed in any preceding claim wherein said polymer is a copolymer of monomers including acrylic acid ester of non-tertiary alkyl alcohol having a chain of 1 to 14 carbon atoms.
10. Pressure-sensitive adhesive tape as claimed in claim 9 wherein the non-tertiary alkyl alcohol molecules contain an average of 4—12 carbon atoms.
11. Pressure-sensitive adhesive tape as claimed in claim 9 or claim 10 wherein said monomers consist essentially of 90—20 parts by weight of said acrylic acid ester of non-tertiary alkyl alcohol and correspondingly 10—80 parts by weight of vinyl carboxylic acid monomer copolymerizable with said acrylic acid ester.
12. Pressure-sensitive adhesive tape as claimed in claim 11 wherein said vinyl carboxylic acid monomer is selected from at least one of acrylic acid, methacrylic acid, and itaconic acid.
13. Pressure-sensitive adhesive tape as claimed in any preceding claim wherein said cations are metal and selected from at least one of Zn, Ti, Fe, and Al.
14. Pressure-sensitive adhesive tape as claimed in any preceding claim which has no backing and wherein a scrim is embedded in and coextensive with said adhesive layer.
15. Pressure-sensitive adhesive tape as claimed in claim 14 wherein said scrim is a cellulose scrim.
16. Pressure-sensitive adhesive tape as claimed in any preceding claim wherein carboxyl groups comprise at least 3.1% by weight of the polymer.
17. Pressure-sensitive adhesive tape as claimed in any preceding claim wherein carboxyl groups comprise up to 22% by weight of the polymer.
18. A method of making substantially tack-free at least one surface of a pressure-sensitive adhesive layer while leaving another surface tacky, which adhesive layer comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, said method comprising applying to said one surface a non-aqueous medium containing a Lewis acid, a polyvalent cation, or a polyvalent organometallic complex or salt to crosslink the polymer along said at least one surface to a substantially tack-free state.
19. A method as claimed in claim 18 wherein said non-aqueous medium is applied to both broad surfaces of said pressure-sensitive adhesive layer.



20. A method of producing substantially tack-free separated mounds on at least one broad surface of a pressure-sensitive adhesive layer while leaving the spacings between the mounds tacky, which adhesive layer comprises a polymer of which carboxyl groups originally comprise at least 1% of the weight, said method comprising applying to the adhesive layer a dot pattern of a non-aqueous medium containing a Lewis acid, a polyvalent cation, or a polyvalent organo-metallic complex or salt to form the mounds and crosslink the polymer at the mounds to a substantially tack-free state.

21. A method as claimed in any of claims 18 to 20 wherein the Lewis acid, polyvalent cation, or organo-metallic complex or salt is dissolved in at least one of methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, and N,N-dimethylformamide.

22. A method as claimed in any of claims 18 to 21 comprising the further step of washing said at least one surface to remove excess cations to stop the crosslinking.

23. A method as claimed in any of claims 18 to 22 wherein carboxyl groups comprise at least 3.1% by weight of the polymer.

24. A method as claimed in any of claims 18 to 23 wherein carboxyl groups comprise up to 22% by weight of the polymer.

25. A method as claimed in any of claims 18 to 24 wherein said polymer is as defined in any of claims 9 to 12.

## 20 Patentansprüche

1. Haftklebeband, dessen Klebstoffschicht mindestens teilweise aus einem Polymer besteht, das ursprünglich mindestens 1 Gew.-% Carboxylgruppen enthält und das auf mindestens einer Oberfläche der Schicht im wesentlichen nichtklebfähig ist, weil es mit mehrwertigen Kationen zwischen Carboxylgruppen vernetzt ist.

2. Haftklebeband, dessen Klebstoffschicht mindestens teilweise aus einem Polymer besteht, das ursprünglich mindestens 1 Gew.-% Carboxylgruppen enthält und das auf einer Breitseitenfläche der Schicht in Abständen voneinander angeordnete, sehr kleine Erhöhungen besitzt, in denen Carboxylgruppen des Polymers mit mehrwertigen Kationen vernetzt sind, während die Zwischenräume zwischen den Erhöhungen unvernetzt und klebfähig geblieben sind.

3. Haftklebeband nach Anspruch 1, dadurch gekennzeichnet, daß mindestens eine Breitseitenfläche der Schicht unvernetzt und klebfähig ist.

4. Haftklebeband nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß eine Randfläche der Schicht mit den Kationen vernetzt und im wesentlichen nichtklebfähig ist.

5. Haftklebeband nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß mindestens eine Breitseitenfläche der Schicht mit den Kationen vernetzt und im wesentlichen nichtklebfähig ist.

6. Haftklebeband nach Anspruch 5, dadurch gekennzeichnet, daß die genannte andere Breitseitenfläche vollkommen nichtklebfähig ist und daß die Klebstoffschicht ohne Rücken auf sich selbst zu einer Rolle aufgewickelt ist.

7. Haftklebeband nach Anspruch 5, oder 6 mit einem schwach haftenden, rückseitigen Überzug, der die nichtklebfähige Breitseitenfläche der Klebstoffschicht bedeckt.

8. Haftklebeband nach einem der Ansprüche 5, 6 und 7, dessen Klebstoffschicht auf beiden Breitseitenflächen in einen im wesentlichen nichtklebfähigen Zustand vernetzt worden ist, wobei ein noch klebfähiger Kern vorhanden ist, der freigelegt werden kann, indem die Klebstoffschicht bis zum Bruch der vernetzten Teile aber ohne Bruch des klebfähigen Kerns gestreckt wird.

9. Haftklebeband nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polymer ein Copolymer aus Monomeren ist, zu denen Acrylsäureester eines nichttertiären Alkylalkohols mit einer Kette mit 1 bis 14 Kohlenstoffatomen gehören.

10. Haftklebeband nach Anspruch 9, dadurch gekennzeichnet, daß die nichttertiären Alkylalkoholmoleküle durchschnittlich 1 bis 12 Kohlenstoffatome enthalten.

11. Haftklebeband nach Anspruch 9 oder 10, dadurch gekennzeichnet, daß die genannten Monomere im wesentlichen aus 90 bis 20 Gewichtsteilen des Acrylsäureesters des nichttertiären Alkylalkohol und entsprechend 10 bis 80 Gewichtsteilen eines mit dem Acrylsäureester copolymerisierbaren Vinylcarbonsäuremonomers bestehen.

12. Haftklebeband nach Anspruch 11, dadurch gekennzeichnet, daß das Vinylcarbonsäuremonomer aus mindestens einer der Substanzen Acrylsäure, Methacrylsäure und Itaconsäure besteht.

13. Haftklebeband nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Kationen aus mindestens einem der Metalle Zn, Ti, Fe und Al bestehen.

14. Haftklebeband nach einem der vorhergehenden Ansprüche, das keinen Rücken besitzt und in dem in der Klebstoffschicht ein mit ihr ausdehnungsgleiches Fadengelege eingebettet ist.

15. Haftklebeband nach Anspruch 14, dadurch gekennzeichnet, daß das Fadengelege aus Cellulose besteht.

16. Haftklebeband nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polymer mindestens 3,1 Gew.-% Carboxylgruppen enthält.

17. Haftklebeband nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polymer bis zu 22 Gew.-% Carboxylgruppen enthält.

18. Verfahren zum Überführen mindestens einer Oberfläche einer Haftkleberschicht in einen im wesentlichen nichtklebfähigen Zustand, während eine andere Oberfläche klebfähig bleibt, wobei die Klebstoffschicht mindestens teilweise aus einem Polymer besteht, das ursprünglich mindestens 1 Gew.-% Carboxylgruppen enthält, und in dem Verfahren zum Vernetzen des Polymers auf der genannten mindestens einen Oberfläche in einen im wesentlichen nichtklebfähigen Zustand auf die genannte Oberfläche ein nichtwäßriges Medium aufgetragen wird, das eine Lewissäure, ein mehrwertiges Kation oder einen mehrwertigen metallorganischen Komplex oder ein mehrwertiges metallorganisches Salz enthält.

19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß das nichtwäßrige Medium auf beide Breitseitenflächen der Haftkleberschicht aufgetragen wird.

20. Verfahren zum Erzeugen von voneinander getrennten, im wesentlichen nicht klebfähigen Erhöhungen auf mindestens einer Breitseitenfläche einer Haftkleberschicht während die Zwischenräume zwischen den Erhöhungen klebfähig bleiben, wobei die Klebstoffschicht mindestens teilweise aus einem Polymer besteht, das ursprünglich mindestens 1 Gew.-% Carboxylgruppen enthält, und in dem Verfahren zum Bilden der Erhöhungen und zum Vernetzen des Polymers an den Erhöhungen in einen im wesentlichen nichtklebfähigen Zustand auf die Klebstoffschicht ein nichtwäßriges Medium aufgetragen wird, das eine Lewissäure, ein mehrwertiges Kation oder einen mehrwertigen metallorganischen Komplex oder ein mehrwertiges metallorganisches Salz enthält.

21. Verfahren nach einem der Ansprüche 18 bis 20, dadurch gekennzeichnet, daß die Lewissäure, das mehrwertige Kation der metallorganische Komplex oder das metallorganische Salz in mindestens einer der Substanzen Methanol, Ethanol, Isopropanol, Aceton, Methyläthylketon und N,N-Dimethylformamid gelöst wird.

22. Verfahren nach einem der Ansprüche 18 bis 21 mit einem weiteren Schritt, in dem die genannte mindestens eine Oberfläche gewaschen wird, um zum Abbruch des Vernetzens überschüssige Kationen zu entfernen.

23. Verfahren nach einem der Ansprüche 18 bis 22, dadurch gekennzeichnet, daß das Polymer mindestens 3,1 Gew.-% Carboxylgruppen enthält.

24. Verfahren nach einem der Ansprüche 18 bis 33, dadurch gekennzeichnet, daß das Polymer höchstens 22 Gew.-% Carboxylgruppen enthält.

25. Verfahren nach einem der Ansprüche 18 bis 24, dadurch gekennzeichnet, daß das Polymer gemäß einem der Ansprüche bis 12 beschaffen ist.

# Revendications

1. Ruban adhésif sensible à la pression dont la couche adhésive comprend un polymère dans lequel les groupes carboxyle comptent initialement au moins pour 1% en poids, le polymère, le long d'au moins une surface de la couche, étant pratiquement non-poisseux du fait qu'il a été réticulé entre les groupes carboxyle par des cations polyvalents.

2. Ruban adhésif sensible à la pression dont la couche adhésive comprend un polymère dans lequel les groupes carboxyle comptent initialement pour au moins 1% en poids, le polymère comportant de petites buttes espacées le long d'une large surface de la couche, où les groupes carboxyle du polymère ont été réticulés par des cations polyvalents, les espaces entre les buttes restant non réticulés et poisseux.

3. Ruban adhésif sensible à la pression selon la revendication 1, dans lequel au moins une large surface de la couche est non-réticulée et poisseuse.

4. Ruban adhésif sensible à la pression selon l'une quelconque des revendications précédentes, dans lequel une surface de bord de la couche est réticulée par lesdits cations et est pratiquement non-poisseuse.

5. Ruban adhésif sensible à la pression selon l'une quelconque des revendications précédentes, dans lequel au moins une large surface de la couche est réticulée par lesdits cations et est pratiquement non-poisseuse.

6. Ruban adhésif sensible à la pression selon la revendication 5, dans lequel ladite autre large surface est entièrement non-poisseuse, et la couche adhésive est enroulée sur elle-même en forme de rouleau, sans support envers.

7. Ruban adhésif sensible à la pression selon la revendication 5 ou la revendication 6, comportant un revêtement d'envers à faible adhérence, qui recouvre ladite large surface non-poisseuse de la couche adhésive.

8. Ruban adhésif sensible à la pression selon l'une quelconque des revendications 5, 6 ou 7, dont la couche adhésive a été réticulée, dans un état pratiquement non-poisseux, aux deux larges surfaces, en laissant un noyau encore poisseux, qui peut être exposé par étirement de la couche adhésive, pour provoquer une rupture des portions réticulées sans rompre le noyau poisseux.

9. Ruban adhésif sensible à la pression selon l'une quelconque des revendications précédentes, dans lequel ledit polymère est un copolymère de monomères comprenant des esters de l'acide acrylique et d'un alcool alkylque non tertiaire ayant une chaîne constituée de 1 à 14 atomes de carbone.

## EP 0 197 662 B1

10. Ruban adhésif sensible à la pression selon la revendication 9, dans lequel les molécules d'alcool alkylique non tertiaire ont en moyenne 4—12 atomes de carbone.

5 11. Ruban adhésif sensible à la pression selon la revendication 9 ou la revendication 10, dans lequel les monomères sont constitués essentiellement de 90 à 20 parties en poids dudit ester de l'acide acrylique d'un alcool alkylique non tertiaire, et en conséquence de 10 à 80 parties en poids d'acide vinylcarboxylique monomère, copolymérisable avec ledit ester de l'acide acrylique.

12. Ruban adhésif sensible à la pression selon la revendication 11, dans lequel ledit acide vinylcarboxylique monomère est choisi parmi l'ensemble comprenant au moins l'acide acrylique, l'acide méthacrylique et l'acide itaconique.

10 13. Ruban adhésif sensible à la pression selon l'une quelconque des revendications précédentes, dans lequel lesdits cations sont des cations métalliques, et sont choisis parmi l'ensemble comprenant les cations Zn, Ti, Fe et Al.

14. Ruban adhésif sensible à la pression selon l'une quelconque des revendications précédentes, qui n'a pas de support envers, et dans lequel est noyé un non-tissé, parallèle à ladite couche adhésive.

15 15. Ruban adhésif sensible à la pression selon la revendication 14, dans lequel ledit non-tissé est un non-tissé de cellulose.

16. Ruban adhésif sensible à la pression selon l'une quelconque des revendications précédentes, dans lequel les groupes carboxyle constituent au moins 3,1% en poids du polymère.

20 17. Ruban adhésif sensible à la pression selon l'une quelconque des revendications précédentes, dans lequel les groupes carboxyle constituent jusqu'à 22% en poids du polymère.

18. Procédé pour rendre pratiquement non-poisseeuse au moins une surface d'une couche adhésive sensible à la pression, tout en laissant poisseuse un autre surface, laquelle couche adhésive comprend un polymère dont les groupes carboxyle constituent initialement au moins 1% du poids, ledit procédé consistant à appliquer sur ladite surface un milieu non-aqueux contenant un acide de Lewis, un cation polyvalent ou un complexe ou un sel organométallique polyvalent, pour réticuler le polymère le long de ladite surface, jusqu'à obtention d'un état pratiquement non-poisseeux.

25 19. Procédé selon la revendication 18, dans lequel ledit milieu non aqueux appliqué sur les deux larges surfaces de ladite couche adhésive sensible à la pression.

20. Procédé pour produire des buttes séparées, pratiquement non-poisseeuses, sur au moins une large surface d'une couche adhésive sensible à la pression, tout en laissant poisseux les espaces entre les buttes, laquelle couche adhésive comprend un polymère dans lequel les groupes carboxyle comptent initialement pour au moins 1% du poids, ledit procédé consistant à appliquer sur la couche adhésive une configuration tramée d'un milieu non aqueux contenant un acide de Lewis, un cation polyvalent ou un complexe ou un sel organométallique polyvalent, pour former les buttes et réticuler le polymère au niveau des buttes pour lui donner un état pratiquement non-poisseeux.

35 21. Procédé selon l'une quelconque des revendications 18 à 20, dans lequel l'acide de Lewis, le cation polyvalent ou le complexe ou le sel organométallique, est dissous dans au moins l'un des solvants suivants: méthanol, éthanol, isopropanol, acétone, méthyléthylcétone et N,N-diméthylformamide.

40 22. Procédé selon l'une quelconque des revendications 18 à 21, comprenant l'étape complémentaire consistant à laver ladite surface pour éliminer les cations en excès, pour arrêter la réticulation.

23. Procédé selon l'une quelconque des revendications 18 à 22, dans lequel les groupes carboxyle constituent au moins 3,1% du poids du polymère.

24. Procédé selon l'une quelconque des revendications 18 à 23, dans lequel les groupes carboxyle constituent jusqu'à 22% du poids du polymère.

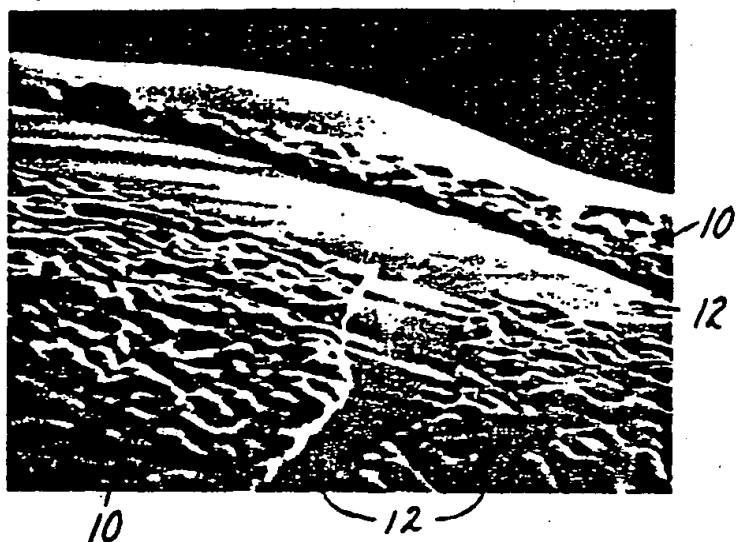
45 25. Procédé selon l'une quelconque des revendications 18 à 24, dans lequel ledit polymère est tel que défini dans l'une quelconque des revendications 9 à 12.

50

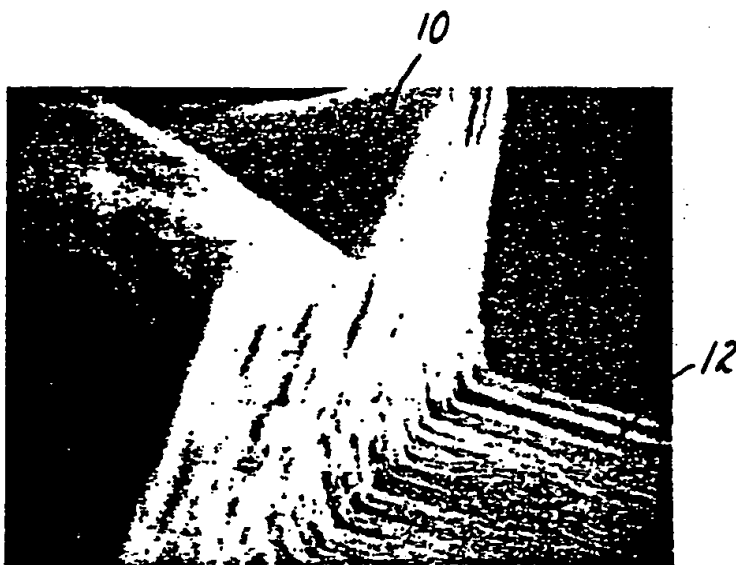
55

60

65



**FIG. 1**



**FIG. 2**

BEST AVAILABLE COPY